

09/937310

JC11 Rec'd PCT/PTO SEP 24 2001

TRANSMITTAL LETTER TO THE UNITED STATES

ATTORNEY'S DOCKET NUMBER 0050/49849

DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

INTERNATIONAL APPLICATION NO.
PCT/EP 00/02610

INTERNATIONAL FILING DATE
28 SEP 2000

PRIORITY DATE CLAIMED
23 MAR 2000

TITLE OF INVENTION: CATALYST COMPRISING A METAL COMPLEX OF THE VIII SUBGROUP BASED ON A PHOSPHINE AMIDITE LIGAND
AND ITS UTILIZATION FOR HYDROFORMYLATION AND HYDROCYANATION

APPLICANT(S) FOR DO/EO/US Wolfgang AHLERS; Heiko MAAS; Michael RÖPER

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2. This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
3. This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. A copy of the International Application as filed (35 U.S.C. 371(c)(2)).

a./ is transmitted herewith (required only if not transmitted by the International Bureau).
b./ has been transmitted by the International Bureau.
c./ is not required, as the application was filed in the United States Receiving Office (RO/USO).
6. A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).

a./ are transmitted herewith (required only if not transmitted by the International Bureau).
b./ have been transmitted by the International Bureau.
c./ have not been made; however, the time limit for making such amendments has NOT expired.
d./ have not been made and will not be made.
8. A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. An oath or declaration of the inventor(s) (35 U.S.C. 171(c)(4)).
10. A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. A FIRST preliminary amendment.
 A SECOND or SUBSEQUENT preliminary amendment.
14. A substitute specification.
15. A change of power of attorney and/or address letter.
16. Other items or information.
International Search Report
International Preliminary Examination Report

09/937310

JC16 Rec'd PCT/PTO SEP 24 2001

U.S. Appln. No. (If Known) INTERNATIONAL APPLN. NO.
PCT/EP 00/02610 ATTORNEY'S DOCKET NO. 0050/49849

17. /X/ The following fees are submitted		<u>CALCULATIONS</u>	<u>PTO USE ONLY</u>
BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):			
Search Report has been prepared by the			
EPO or JPO.....	\$860.00	860.00	
International preliminary examination fee paid to USPTO (37 CFR 1.482).....	\$690.00		
No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)).....	\$710.00		
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO	\$1000.00		
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied pro -visions of PCT Article 33(2)-(4).....	\$100.00		
ENTER APPROPRIATE BASIC FEE AMOUNT =	\$ 860.00		
Surcharge of \$130.00 for furnishing the oath or declaration later than / / 20 / / 30 months from the earliest claimed priority date (37 CFR 1.492(e)).			
<u>Claims</u>	<u>Number Filed</u>	<u>Number Extra</u>	<u>Rate</u>
Total Claims	-20		X\$18.
Indep. Claims	-3		X\$80.
Multiple dependent claim(s)(if applicable)			+270.
<u>TOTAL OF ABOVE CALCULATION</u>		=	
Reduction of $\frac{1}{2}$ for filing by small entity, if applicable. Verified Small Entity statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28).			
<u>SUBTOTAL</u>		=	860.00
Processing fee of \$130. for furnishing the English translation later than / / 20 / / 30 months from the earliest claimed priority date (37 CFR 1.492(f)). +			
<u>TOTAL NATIONAL FEE</u>		=	860.00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) \$40.00 per property =			40.00
<u>TOTAL FEES ENCLOSED</u>		=	\$ 900.00

Amount to be
refunded: \$
Charged: \$

a./X/ A check in the amount of \$900.00 to cover the above fees is enclosed.

b./ / Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c./X/ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 11-0345. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b) must be filed and granted to restore the application to pending status.

Herbert B. Keil

SEND ALL CORRESPONDENCE TO:
 KEIL & WEINKAUF

1101 Connecticut Ave., N.W.
 Washington, D. C. 20036

SIGNATURE

Herbert B. Keil
 NAME
18,967
 Registration No.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of)
AHLERS et al.) BOX PCT
PCT/EP 00/02610)
Intl. Filing Date: March 23, 2000)
US Serial No.: TO BE ASSIGNED)
)
For: CATALYST COMPRISING A METAL COMPLEX OF THE VIII SUBGROUP
BASED ON A PHOSPHINE AMIDITE LIGAND AND ITS UTILIZATION FOR
HYDROFORMYLATION AND HYDROCYANATION

Honorable Commissioner of
Patents and Trademarks
Washington, D.C. 20231

PRELIMINARY AMENDMENT

Sir:

Prior to examination of the above-identified U.S. National
Stage application, kindly amend the application as follows.

REMARKS

Attached is a clean set of all claims, as well as a marked up version of the amended claims. The claims have been amended to eliminate multiple dependency and to place them in better form for U.S. practice. Favorable action on the application is solicited.

Respectfully submitted,

KEIL & WEINKAUF



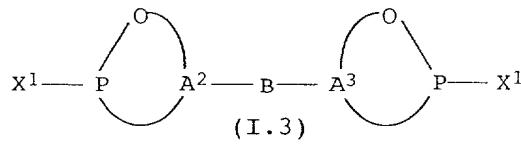
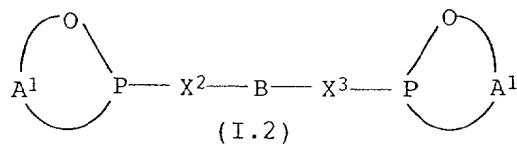
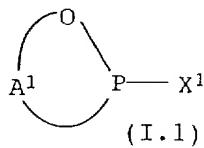
Herbert B. Keil
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1101 Connecticut Avenue, N.W.
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HBK/kas

CLEAN VERSION OF ALL CLAIMS

1. A catalyst comprising at least one complex of a metal of transition group VIII comprising at least one monodentate, bidentate or multidentate phosphinamidite ligand of the formulae I.1, I.2 and/or I.3



where

A¹ together with the phosphorus atom and the oxygen atom to which it is bound form a 5- to 8-membered heterocycle onto which one, two or three cycloalkyl, aryl and/or hetaryl groups may be fused, where the fused-on groups may each bear, independently of one another, one, two or three substituents selected from among alkyl, alkoxy, halogen, nitro, cyano, carboxyl and carboxylate,

A² and A³ are, independently of one another, part of a

heterocycle as defined for A¹ which is substituted by B,
X¹ is a 5- to 8-membered heterocycle which contains at least
one nitrogen atom bound directly to the phosphorus atom,
where the heterocycle may additionally contain one or two
heteroatom(s) selected from among N, O and S and/or one, two
or three cycloalkyl, aryl and/or hetaryl groups may be fused
onto the heterocycle, where the heterocycle and/or the
fused-on groups may each bear, independently of one another,
one, two or three substituents selected from among alkyl,
cycloalkyl, aryl, alkoxy, cycloalkoxy, aryloxy, acyl,
halogen, trifluoromethyl, nitro, cyano, carboxyl,
carboxylate, alkoxycarbonyl and NE¹E², where E¹ and E² may be
identical or different and are each alkyl, cycloalkyl or
aryl,

X² and X³ are, independently of one another, a heterocycle as
defined for X¹ which is substituted by B,

B is either a carbon-carbon single bond or a divalent bridging
group,

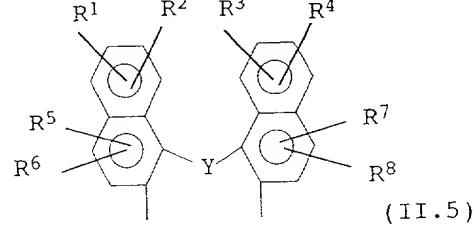
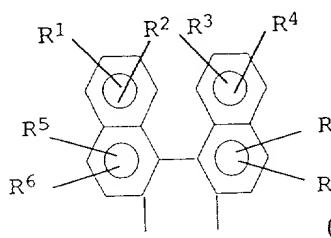
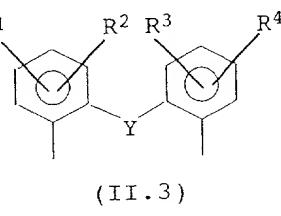
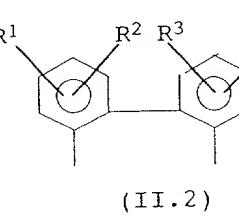
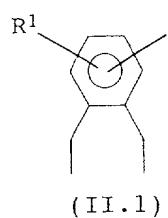
or salts or mixtures thereof.

2. A catalyst as claimed in claim 1, wherein B is a
bridging group of the formula -D-, -(CO)-D-(CO)- or -(CO)-(CO)-,
in which

D is a C₁-C₁₀-alkylene bridge which may have one, two, three or
four double bonds and/or bear one, two, three or four
substituents selected from among alkyl, alkoxy, halogen,

nitro, cyano, carboxyl, carboxylate, cycloalkyl and aryl, where the aryl substituent may additionally bear one, two or three substituents selected from among alkyl, alkoxy, halogen, trifluoromethyl, nitro, alkoxycarbonyl or cyano, and/or the alkylene bridge D may be interrupted by one, two or three nonadjacent, substituted or unsubstituted heteroatoms, and/or the alkylene bridge D may have one, two or three aryl and/or hetaryl groups fused onto it, where the fused-on aryl and hetaryl groups may each bear one, two or three substituents selected from among alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy, aryloxy, aryl, halogen, trifluoromethyl, nitro, cyano, carboxyl, alkoxycarbonyl and NE^1E^2 , where E^1 and E^2 may be identical or different and are each alkyl, cycloalkyl or aryl.

3. A catalyst as claimed in claim 2, wherein D is a radical of the formula II.1, II.2, II.3, II.4 or II.5



where

Y is O, S, NR⁹, where

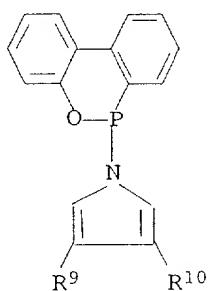
R⁹ is alkyl, cycloalkyl or aryl,

or Y is a C₁-C₃-alkylene bridge which may have a double bond and/or an alkyl, cycloalkyl- or aryl substituent, where the aryl substituent may bear one, two or three substituents selected from among alkyl, alkoxy, halogen, trifluoromethyl, nitro, alkoxycarbonyl and cyano,

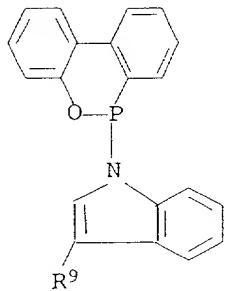
or Y is a C₂-C₃-alkylene bridge which is interrupted by O, S or NR⁹,

R¹, R², R³, R⁴, R⁵, R⁶, R⁷ and R⁸ are, independently of one another hydrogen, alkyl, cycloalkyl, aryl, alkoxy, halogen, trifluoromethyl, nitro, alkoxycarbonyl or cyano.

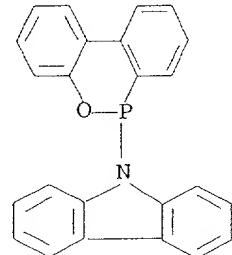
4. (amended) A catalyst as claimed in claim 1, wherein the phosphinamidite ligand is selected from among the ligands of the formulae IIIa to IIII



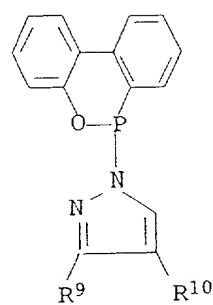
(IIIa)



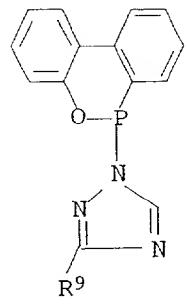
(IIIb)



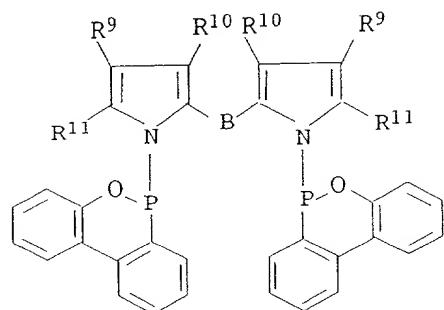
(IIIc)



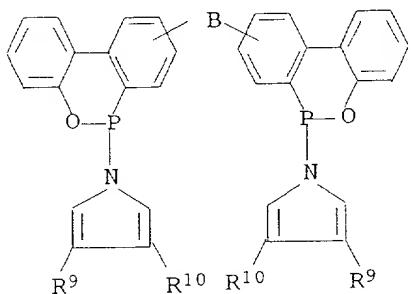
(III d)



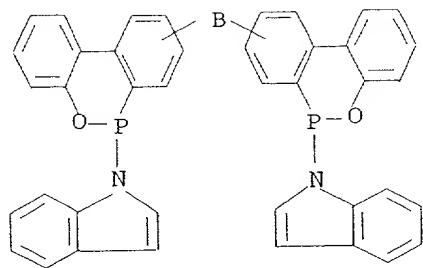
(III e)



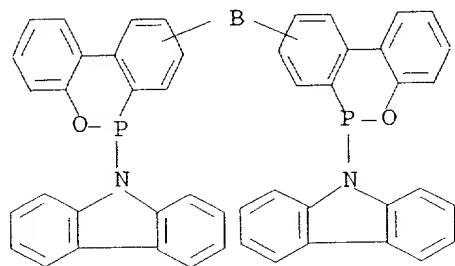
(III f)



(III g)



(IIIh)



(IIIf)

where

R^9 and R^{10} are, independently of one another, hydrogen, methyl, ethyl or trifluoromethyl,

R^{11} is hydrogen or $COOC_2H_5$,

B is CH_2 , $C(CH_3)_2$, $(CO)-(CO)$ or $(CO)-D-(CO)$,

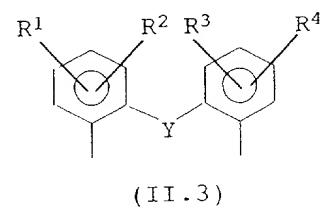
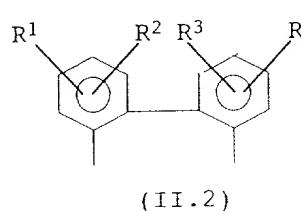
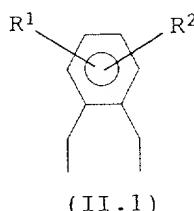
where B in the formulae IIIg, IIIh and IIIf can in each case

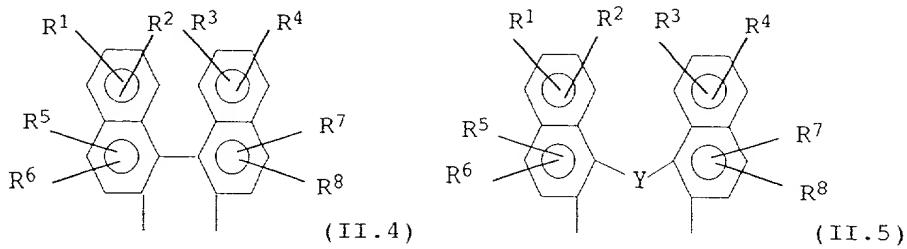
be bound in the o,o positions, m,m positions or p,p positions relative to the phosphorus atoms and

D is a C_1-C_{10} - alkylene bridge which may have one, two, three or four double bonds and/or bear one, two, three or four substituents selected from

among alkyl, alkoxy, halogen, nitro, cyano, carboxyl, carboxylate, cycloalkyl and aryl, where the aryl substituent may additionally bear one, two or three substituents selected from among alkyl, alkoxy, halogen, trifluoromethyl, nitro, alkoxycarbonyl or cyano, and/or the alkylene bridge D may be interrupted by one, two or three nonadjacent, substituted or unsubstituted heteroatoms, and/or the alkylene bridge D may have one, two or three aryl and/or hetaryl groups fused onto it, where the fused-on aryl and hetaryl groups may each bear one, two or three substituents selected from among alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy, aryloxy, aryl, halogen, trifluoromethyl, nitro, cyano, carboxyl, alkoxycarbonyl and NE^1E^2 , where E^1 and E^2 may be identical or different and are each alkyl, cycloalkyl or aryl, or

D is a radical of the formula II.1, II.2, II.3, II.4 or II.5





where

Y is O, S, NR⁹, where

R⁹ is alkyl, cycloalkyl or aryl,

or Y is a C₁-C₃-alkylene bridge which may have a double bond and/or an alkyl, cycloalkyl- or aryl substituent, where the aryl substituent may bear one, two or three substituents selected from among alkyl, alkoxy, halogen, trifluoromethyl, nitro, alkoxycarbonyl and cyano,

or Y is a C₂-C₃-alkylene bridge which is interrupted by O, S or NR⁹,

R¹, R², R³, R⁴, R⁵, R⁶, R⁷ and R⁸ are, independently of one another hydrogen, alkyl, cycloalkyl, aryl, alkoxy, halogen, trifluoromethyl, nitro, alkoxycarbonyl or cyano.

5. (amended) A catalyst as claimed in claim 1, wherein the metal of transition group VIII is selected from among cobalt, ruthenium, iridium, rhodium, nickel, palladium and platinum.

6. (amended) A catalyst as claimed in claim 1 which further comprises at least one further ligand selected from among halides, amines, carboxylates, acetylacetone, arylsulfonates or alkylsulfonates, hydride, CO, olefins, dienes, cycloolefins, nitriles, N-containing heterocycles, aromatics and heteroaromatics, ethers, PF₃, and monodentate, bidentate and multidentate phosphine, phosphinite, phosphonite and phosphite ligands.

7. (amended) A process for the hydroformylation of compounds which contain at least one ethylenically unsaturated double bond by reaction with carbon monoxide and hydrogen in the presence of a hydroformylation catalyst, wherein the hydroformylation catalyst used is a catalyst as claimed in claim 1.

8. (amended) A process for the hydrocyanation of compounds containing at least one ethylenically unsaturated double bond by reaction with hydrogen cyanide in the presence of a hydrocyanation catalyst, wherein the hydrocyanation catalyst used is a catalyst as claimed in claim 1.

9. (amended) A process as claimed in claim 7, wherein the hydroformylation catalyst or the hydrocyanation catalyst is prepared in situ by reacting at least one phosphinamidite ligand, a compound or a complex of a metal of transition group VIII and, if desired, an activator in an inert solvent under the hydroformylation conditions or the hydrocyanation conditions.

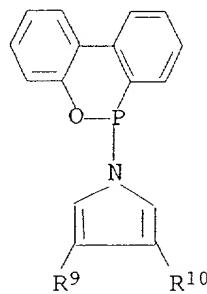
10. (amended) The use of a catalyst comprising a

phosphinamidite ligand as claimed in claim 1 for the hydroformylation or hydrocyanation of compounds having at least one ethylenically unsaturated double bond.

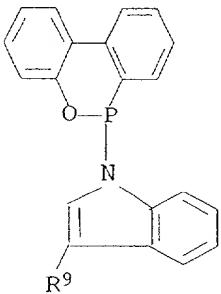
VERSION WITH MARKINGS TO SHOW CHANGES MADE

Amend claims 4 - 10 as follows:

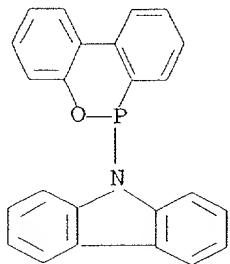
4. (amended) A catalyst as claimed in [any of the preceding claims] claim 1, wherein the phosphinamidite ligand is selected from among the ligands of the formulae IIIa to IIIi



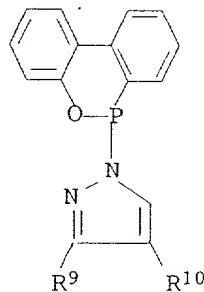
(IIIa)



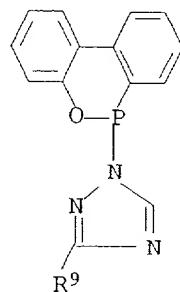
(IIIb)



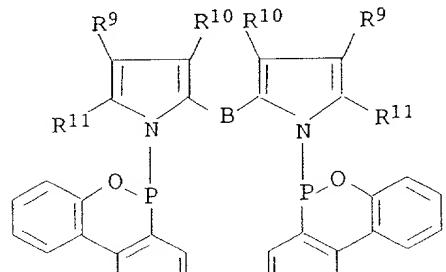
(IIIc)



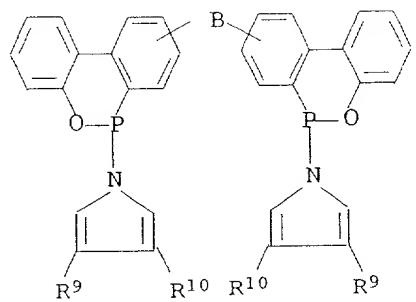
(IId)



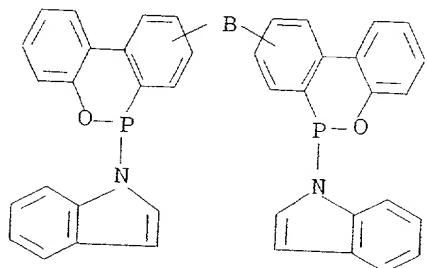
(IIIf)



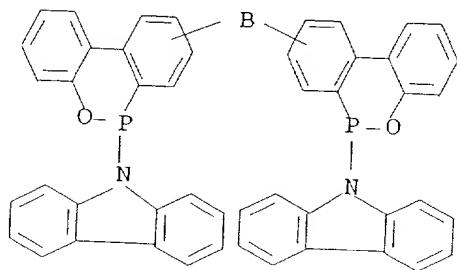
(IIIf)



(IIIg)



(IIIh)



(IIIi)

where

R^9 and R^{10} are, independently of one another, hydrogen, methyl, ethyl or trifluoromethyl,

R^{11} is hydrogen or $COOC_2H_5$,

B is CH_2 , $C(CH_3)_2$, $(CO)-(CO)$ or $(CO)-D-(CO)$,

where B in the formulae IIIg, IIIh and IIIi can in each case be bound in the o,o positions, m,m positions or p,p positions relative to the phosphorus atoms and

D is a C_1-C_{10} - alkylene bridge [as defined in claim 2 or 3] which may have one, two, three or four

double bonds and/or bear one, two, three or four

substituents selected from among alkyl, alkoxy,

halogen, nitro, cyano, carboxyl, carboxylate,

cycloalkyl and aryl, where the aryl substituent

may additionally bear one, two or three

substituents selected from among alkyl, alkoxy,

halogen, trifluoromethyl, nitro, alkoxy carbonyl or

cyano, and/or the alkylene bridge D may be

interrupted by one, two or three nonadjacent,

substituted or unsubstituted heteroatoms, and/or

the alkylene bridge D may have one, two or three

aryl and/or hetaryl groups fused onto it, where

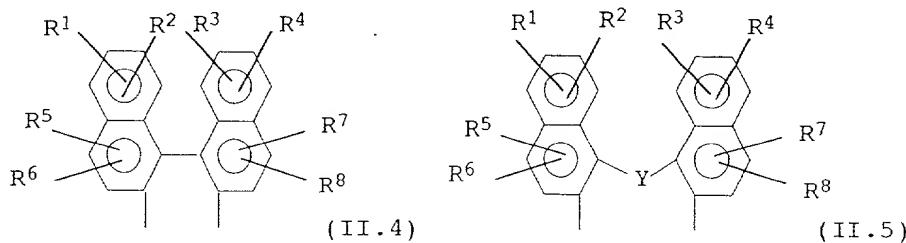
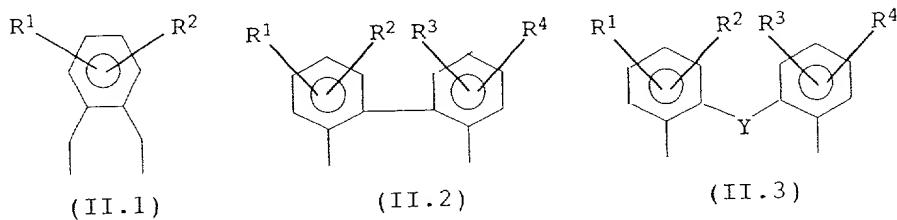
the fused-on aryl and hetaryl groups may each bear

one, two or three substituents selected from among

alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy,

aryloxy, aryl, halogen, trifluoromethyl, nitro,
cyano, carboxyl, alkoxy carbonyl and NE¹E², where E¹
and E² may be identical or different and are each
alkyl, cycloalkyl or aryl, or

D is a radical of the formula II.1, II.2, II.3, II.4 or II.5



where

Y is O, S, NR⁹, where

R⁹ is alkyl, cycloalkyl or aryl,

or Y is a C_1 - C_3 -alkylene bridge which may have a double bond and/or an alkyl, cycloalkyl- or aryl substituent, where the aryl substituent may bear one, two or three substituents

selected from among alkyl, alkoxy, halogen,
trifluoromethyl, nitro, alkoxycarbonyl and
cyano,

or Y is a C₂-C₃-alkylene bridge which is
interrupted by O, S or NR⁹,
R¹, R², R³, R⁴, R⁵, R⁶, R⁷ and R⁸ are, independently
of one another hydrogen, alkyl,
cycloalkyl, aryl, alkoxy, halogen,
trifluoromethyl, nitro, alkoxycarbonyl
or cyano.

5. (amended) A catalyst as claimed in [any of the preceding claims] claim 1, wherein the metal of transition group VIII is selected from among cobalt, ruthenium, iridium, rhodium, nickel, palladium and platinum.

6. (amended) A catalyst as claimed in [any of the preceding claims] claim 1 which further comprises at least one further ligand selected from among halides, amines, carboxylates, acetylacetone, arylsulfonates or alkylsulfonates, hydride, CO, olefins, dienes, cycloolefins, nitriles, N-containing heterocycles, aromatics and heteroaromatics, ethers, PF₃ and monodentate, bidentate and multidentate phosphine, phosphinite, phosphonite and phosphite ligands.

7. (amended) A process for the hydroformylation of compounds which contain at least one ethylenically unsaturated double bond by reaction with carbon monoxide and hydrogen in the presence of

a hydroformylation catalyst, wherein the hydroformylation catalyst used is a catalyst as claimed in [any of claims 1 to 6] claim 1.

8. (amended) A process for the hydrocyanation of compounds containing at least one ethylenically unsaturated double bond by reaction with hydrogen cyanide in the presence of a hydrocyanation catalyst, wherein the hydrocyanation catalyst used is a catalyst as claimed in [any of claims 1 to 6] claim 1.

9. (amended) A process as claimed in claim 7 [or 8], wherein the hydroformylation catalyst or the hydrocyanation catalyst is prepared in situ by reacting at least one phosphinamidite ligand [as defined in any of claims 1 to 6], a compound or a complex of a metal of transition group VIII and, if desired, an activator in an inert solvent under the hydroformylation conditions or the hydrocyanation conditions.

10. (amended) The use of a catalyst comprising a phosphinamidite ligand as claimed in [any of claims 1 to 6] claim 1 for the hydroformylation or hydrocyanation of compounds having at least one ethylenically unsaturated double bond.

Catalyst comprising a metal complex of the VIII subgroup based on a phosphine amidite ligand and its utilization for hydroformylation and hydrocyanation

5

The present invention relates to a catalyst comprising at least one complex of a metal of transition group VIII comprising at least one monodentate, bidentate or multidentate phosphinamidite ligand, and also processes for the hydroformylation and

10 hydrocyanation of compounds containing at least one ethylenically unsaturated double bond in the presence of such a catalyst.

Hydroformylation, also known as the oxo process, is an important industrial process and is employed for the preparation of

15 aldehydes from olefins, carbon monoxide and hydrogen. If desired, these aldehydes can be hydrogenated by means of hydrogen in the same process step to form the corresponding oxo alcohols. The reaction itself is strongly exothermic and generally proceeds under superatmospheric pressure at elevated temperatures in the 20 presence of catalysts. Catalysts used are Co, Rh, Ir, Ru, Pd or Pt compounds or complexes which can be modified with N- or P-containing ligands to influence the activity and/or selectivity. Owing to the possible addition of CO onto each of the two carbon atoms of a double bond, the hydroformylation

25 reaction forms mixtures of isomeric aldehydes. In addition, double bond isomerization can also occur. In these isomeric mixtures, the n-aldehyde is frequently formed preferentially compared to the iso-aldehyde, and, owing to the significantly greater industrial importance of the n-aldehydes, attempts are 30 made to optimize the hydroformylation catalysts so as to achieve a greater n-selectivity.

Beller et al., Journal of Molecular Catalysis A, 104 (1995), pages 17-85, describes rhodium-containing, phosphine-modified 35 catalysts for the hydroformylation of low-boiling olefins.

Disadvantages of these catalysts are that they can only be prepared using organometallic reagents and that the ligands used are complicated and expensive to prepare. In addition, the hydroformylation of internal straight-chain and branched olefins 40 and also of olefins having more than 7 carbon atoms is very slow when these phosphine-modified catalysts are used.

WO 95/30680 describes bidentate phosphine ligands in which the two phosphine groups are each bound to an aryl radical and these 45 two aryl radicals form a doubly bridged, ortho-fused ring system in which one of the two bridges consists of an oxygen or sulfur atom. Rhodium complexes based on these ligands are suitable as

hydroformylation catalysts, with a good n/iso ratio being achieved in the hydroformylation of terminal olefins. A disadvantage of these chelating phosphines is their complicated preparation, so that industrial processes based on such chelating 5 phosphine catalysts have an economic disadvantage.

US-A-4,169,861 describes a process for preparing terminal aldehydes by hydroformylation of α -olefins in the presence of a rhodium hydroformylation catalyst based on one bidentate ligand 10 and one monodentate ligand. As bidentate ligand, preference is given to using 1,1'-bis(diphenylphosphino)ferrocene. The monodentate ligand is preferably a phosphine such as diphenylethylphosphine. US-A-4,201,714 and US-A-4,193,943 make similar disclosures. The preparation of the bidentate 15 phosphinoferrocene ligands requires the use of organometallic reactions which are complicated to prepare, as a result of which hydroformylation processes using these catalysts have an economic disadvantage.

20 US-A-5,312,996 describes a process for preparing 1,6-hexanodial by hydroformylation of butadiene in the presence of hydrogen and carbon monoxide. Hydroformylation catalysts used are rhodium complexes having polyphosphite ligands in which the phosphorus and two of the oxygen atoms of the phosphite group are part of a 25 7-membered heterocycle.

JP-A 97/255 610 describes a process for preparing aldehydes by hydroformylation in the presence of rhodium catalysts which have a monodentate phosphonite ligand.

30 The catalytic hydrocyanation for producing nitriles from olefins is likewise of great industrial importance.

35 In "Applied Homogeneous Catalysis with Organometallic Compounds", Vol. 1, VCH Weinheim, p. 465 ff., the heterogeneously and homogeneously catalyzed addition of hydrogen cyanide onto olefins is described in general terms. Here, use is made, in particular, of catalysts based on phosphine, phosphite and phosphonite 40 complexes of nickel and palladium.

In Organometallics 1984, 3, p. 33 ff., C. A. Tolman et al. describe the catalytic hydrocyanation of olefins in the presence of nickel(0)-phosphite complexes with special reference to the 45 effects of Lewis acids on the hydrogen cyanide addition.

In Advances in Catalysis, Volume 33, 1985, Academic Press Inc., p. 1 ff., a review of the homogeneously nickel-catalyzed hydrocyanation of olefins is given. Catalysts used are nickel(0) complexes comprising phosphine and phosphite ligands.

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None of the abovementioned literature references describes hydroformylation catalysts or hydrocyanation catalysts based on monodentate, bidentate or multidentate phosphinamidite ligands in which the phosphorus atom and the oxygen atom of the

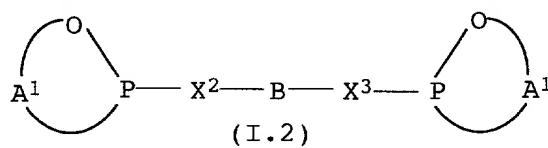
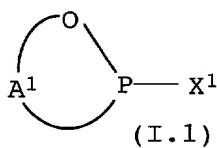
10 phosphinamidite group are part of a 5- to 8-membered heterocycle.

It is an object of the present invention to provide new catalysts based on complexes of a metal of transition group VIII. These 15 should preferably be suitable for hydroformylation or hydrocyanation reactions and have a good catalytic activity.

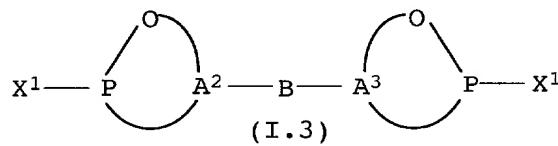
We have found that this object is achieved by catalysts based on complexes of a metal of transition group VIII which comprise at 20 least one monodentate, bidentate or multidentate phosphinamidite ligand in which the phosphorus atom and the oxygen atom of the phosphinamidite group are part of a 5- to 8-membered heterocycle.

25 The present invention accordingly provides a catalyst comprising at least one complex of a metal of transition group VIII comprising at least one monodentate, bidentate or multidentate phosphinamidite ligand of the formulae I.1, I.2 and/or I.3

30



35



40

where

A¹ together with the phosphorus atom and the oxygen atom to which it is bound form a 5- to 8-membered heterocycle onto which one, two or three cycloalkyl, aryl and/or 45 hetaryl groups may be fused, where the fused-on groups may each bear, independently of one another, one, two or

three substituents selected from among alkyl, alkoxy, halogen, nitro, cyano, carboxyl and carboxylate,

5 A² and A³ are, independently of one another, part of a heterocycle as defined for A¹ which is substituted by B,

10 x¹ is a 5- to 8-membered heterocycle which contains at least one nitrogen atom bound directly to the phosphorus atom, where the heterocycle may additionally contain one or two heteroatom(s) selected from among N, O and S and/or one, two or three cycloalkyl, aryl and/or hetaryl groups may be fused onto the heterocycle, where the heterocycle and/or the fused-on groups may each bear, independently of one another, one, two or three substituents selected from among alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy, aryloxy, acyl, halogen, trifluoromethyl, nitro, cyano, carboxyl, carboxylate, alkoxy carbonyl and NE¹E², where E¹ and E² may be identical or different and are each alkyl, cycloalkyl or aryl,

20 x² and x³ are, independently of one another, a heterocycle as defined for X¹ which is substituted by B,

25 B is either a carbon-carbon single bond or a divalent bridging group,

or salts or mixtures thereof.

For the purposes of the present invention, the expression "alkyl" includes both straight-chain and branched alkyl groups. Preferred alkyl groups are straight-chain or branched C₁-C₈-alkyl groups, preferably C₁-C₆-alkyl groups and particularly preferably C₁-C₄-alkyl groups. Examples of alkyl groups are, in particular, methyl, ethyl, propyl, isopropyl, n-butyl, 2-butyl, sec-butyl, 35 tert-butyl, n-pentyl, 2-pentyl, 2-methylbutyl, 3-methylbutyl, 1,2-dimethylpropyl, 1,1-dimethylpropyl, 2,2-dimethylpropyl, 1-ethylpropyl, n-hexyl, 2-hexyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 2,3-dimethylbutyl, 1,1-dimethylbutyl, 2,2-dimethylbutyl, 40 3,3-dimethylbutyl, 1,1,2-trimethylpropyl, 1,2,2-trimethylpropyl, 1-ethylbutyl, 2-ethylbutyl, 1-ethyl- 2-methylpropyl, n-heptyl, 2-heptyl, 3-heptyl, 2-ethylpentyl, 1-propylbutyl, octyl.

The cycloalkyl group is preferably a C₅-C₇-cycloalkyl group such 45 as cyclopentyl, cyclohexyl or cycloheptyl.

If the cycloalkyl group is substituted, it preferably bears 1, 2, 3, 4 or 5 substituents, in particular 1, 2 or 3 substituents, selected from among alkyl, alkoxy and halogen.

5 Aryl is preferably phenyl, tolyl, xylyl, mesityl, naphthyl, anthracenyl, phenanthrenyl, naphthacenyl and in particular phenyl or naphthyl.

Substituted aryl radicals preferably have 1, 2, 3, 4 or 5
10 substituents, in particular 1, 2 or 3 substituents, selected from among alkyl, alkoxy, carboxyl, carboxylate, trifluoromethyl, nitro, cyano and halogen.

Hetaryl is preferably pyridyl, quinolinyl, acridinyl,
15 pyridazinyl, pyrimidinyl or pyrazinyl.

Substituted hetaryl radicals preferably bear, 1, 2 or 3 substituents selected from among alkyl, alkoxy, trifluoromethyl and halogen.

20 The above details regarding alkyl, cycloalkyl and aryl radicals apply analogously to alkoxy, cycloalkoxy and aryloxy radicals.

The radicals NE^1E^2 are preferably N,N-dimethyl, N,N-diethyl,
25 N,N-dipropyl, N,N-diisopropyl, N,N-di-n-butyl, N,N-di-t-butyl, N,N-dicyclohexyl or N,N-diphenyl.

Halogen is fluorine, chlorine, bromine or iodine, preferably fluorine, chlorine or bromine.

30 For the purposes of the present invention, carboxylate is preferably a derivative of a carboxylic acid function, in particular a metal carboxylate, a carboxylic ester function or a carboxamide function, particularly preferably a carboxylic ester
35 function. This includes, for example, esters of C₁-C₄-alkanols such as methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol and tert-butanol.

The radicals A¹ in the formulae I.1 and I.2 and the radicals A²
40 and A³ in the formula I.3, in each case together with the phosphorus atom and the oxygen atom of the phosphinamidite group to which they are bound, preferably form a 5- to 8-membered heterocycle to which one or two aryl and/or hetaryl groups may be fused.

45 The fused-on aryls of the radicals A¹, A² and/or A³ are preferably benzene or naphthalene, in particular benzene.

The fused-on aryls and/or hetaryl of the radicals A¹, A² and/or A³ are preferably unsubstituted or each have 1, 2 or 3 substituents, in particular 1 or 2 substituents, which are selected from among alkyl, alkoxy, trifluoromethyl, halogen, nitro, cyano, carboxyl and carboxylate.

A¹ is preferably a 2,2'-biphenylene, 2,2'-binaphthylene or 2,3-xylylene radical which may bear 1, 2 or 3 substituents selected from among alkyl, alkoxy, trifluoromethyl, carboxylate or halogen. Here, alkyl is preferably C₁-C₄-alkyl and in particular t-butyl. Alkoxy is preferably C₁-C₄-alkoxy and in particular methoxy. Halogen is in particular fluorine, chlorine or bromine.

15

Radicals A² and A³ are preferably each a 2,2'-biphenylene radical. The radicals A² and A³ preferably bear the bridging group B in the para position relative to the phosphorus atom or the oxygen atom of the phosphinamidite group.

20

The radicals X¹ in the formulae I.1 and I.3 and the radicals X² and X³ in the formula I.2 are preferably each a 5- or 6-membered heterocycle containing at least one nitrogen atom which is bound directly to the phosphorus atom to form a phosphinamidite group.

Preferred radicals X¹, X² and/or X³ can additionally contain one or two hetero atom(s) selected from among N, O and S. The additional heteroatoms are preferably nitrogen atoms. Preferred radicals X¹, X² and/or X³ additionally have one or two aryl and/or hetaryl groups fused onto them. Unfused heterocycles are preferably unsubstituted or may bear one, two or three substituents selected from among alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy, aryloxy, acyl, halogen, trifluoromethyl, nitro, cyano, carboxyl, carboxylate, alkoxy carbonyl and NE¹E², where E¹ and E² may be identical or different and are alkyl, cycloalkyl or aryl. In the case of singly fused radicals X¹, X² and/or X³ the heterocycle is preferably unsubstituted or has one of the abovementioned substituents on the heterocycle. In the case of singly fused and doubly fused radicals X¹, X² and/or X³, the fused-on rings preferably each have, independently of one another, 1, 2 or 3, in particular 1 or 2, of the abovementioned substituents.

The radicals X¹, X² and X³ are preferably selected from among aromatic heterocycles.

45

If the radicals X¹, X² and/or X³ bear fused-on aryls, the latter are preferably benzene or naphthalene, in particular benzene.

The radicals X^1 , X^2 and X^3 are preferably selected, independently of one another, from among 1-pyrrolyl, 1-pyrazolyl, 1-imidazolyl, 1-triazolyl, 1-indyl, 1-indazolyl, 7-purinyl, 2-isoindyl and 9-carbazolyl which may each bear one, two or three of the 5 abovementioned substituents.

The radicals X^2 and X^3 are preferably each a 1-pyrrolyl radical which has the bridging group B in the 2 position or in the 3 position, in particular in the 2 position. In addition, it may 10 bear one, two or three of the abovementioned substituents in the 3, 4 and/or 5 position.

The bridging group B is preferably a carbon-carbon single bond or a divalent bridging group having from 1 to 15 atoms in the chain 15 between the flanking compounds.

B is preferably a bridging group of the formula -D-, -(CO)-D-(CO)- or -(CO)-(CO)-, in which

20 D is a C_1-C_{10} -alkylene bridge which may have one, two, three or four double bonds and/or bear one, two, three or four substituents selected from among alkyl, alkoxy, halogen, nitro, cyano, carboxyl, carboxylate, cycloalkyl and aryl, where the aryl substituent may additionally bear one, two or 25 three substituents selected from among alkyl, alkoxy, halogen, trifluoromethyl, nitro, alkoxycarbonyl or cyano, and/or the alkylene bridge D may be interrupted by one, two or three nonadjacent, substituted or unsubstituted heteroatoms, and/or the alkylene bridge D may have one, two or 30 three aryl and/or hetaryl groups fused onto it, where the fused-on aryl and hetaryl groups may each bear one, two or three substituents selected from among alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy, aryloxy, acyl, halogen, trifluoromethyl, nitro, cyano, carboxyl, alkoxycarbonyl and 35 NE^1E^2 , where E^1 and E^2 may be identical or different and are each alkyl, cycloalkyl or aryl.

The radical D is preferably a C_1-C_8 -alkylene bridge which, depending on the number of carbon atoms, has 1, 2 or 3 aryl 40 groups fused onto it and/or may bear 1, 2, 3 or 4 substituents selected from among alkyl, cycloalkyl and substituted or unsubstituted aryl, and/or may additionally be interrupted by 1, 2 or 3 substituted or unsubstituted heteroatoms.

45 The fused-on aryls of the radical D are preferably benzene or naphthalene, in particular benzene. Fused-on benzene rings are preferably unsubstituted or have 1, 2 or 3, in particular 1 or 2,

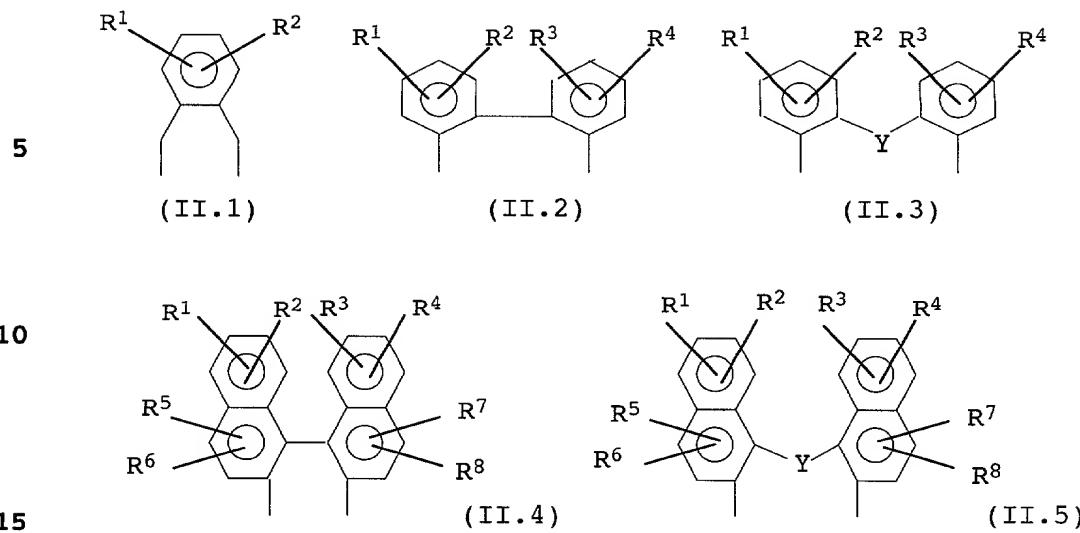
substituents selected from among alkyl, alkoxy, halogen, trifluoromethyl, nitro, carboxyl, alkoxycarbonyl and cyano. Fused-on naphthalenes are preferably unsubstituted or bear, in the ring which is not fused on and/or in the fused-on ring, in 5 each case 1, 2 or 3, in particular 1 or 2, of the substituents mentioned above for the fused-on benzene rings. These are then preferably alkyl or alkoxycarbonyl. In the case of the substituents of the fused-on aryls, alkyl is preferably C₁-C₄-alkyl and in particular methyl, isopropyl and tert-butyl. 10 Alkoxy is preferably C₁-C₄-alkoxy and in particular methoxy. Alkoxycarbonyl is preferably C₁-C₄-alkoxycarbonyl. Halogen is in particular fluorine or chlorine.

If the alkylene bridge of the radical D is interrupted by 1, 2 or 15 3 substituted or unsubstituted heteroatoms, these are preferably selected from among O, S and NR¹⁰, where R¹⁰ is alkyl, cycloalkyl or aryl.

If the alkylene bridge of the radical D is substituted, it bears 20 1, 2, 3 or 4 substituents which is/are preferably selected from among alkyl, cycloalkyl and aryl, where the aryl substituent may additionally bear 1, 2 or 3 substituents selected from among alkyl, alkoxy, halogen, trifluoromethyl, nitro, alkoxycarbonyl and cyano. The substituents of the alkylene bridge D are 25 preferably selected from among methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, phenyl, p-(C₁-C₄-alkyl)phenyl, preferably p-methylphenyl, p-(C₁-C₄-alkoxy)phenyl, preferably p-methoxyphenyl, p-halophenyl, preferably p-chlorophenyl and p-trifluoromethylphenyl.

30 In a preferred embodiment, D is an unfused C₁-C₇-alkylene bridge which is substituted and/or interrupted by substituted or unsubstituted heteroatoms, as described above. In particular, the radical D is a C₁-C₅-alkylene bridge bearing 1, 2, 3 or 4 35 substituents selected from among methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl and phenyl.

In a further, preferred embodiment, D is a radical of the formula II.1, II.2, II.3, II.4 or II.5



where

Y is O, S, NR⁹, where
R⁹ is alkyl, cycloalkyl or aryl,

or Y is a C₁-C₃-alkylene bridge which may have a double bond and/or an alkyl, cycloalkyl- or aryl substituent, where the aryl substituent may bear one, two or three substituents selected from among alkyl, alkoxy, halogen, trifluoromethyl, nitro, alkoxy carbonyl and cyano,

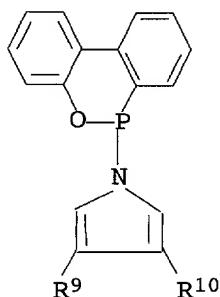
or Y is a C₂-C₃-alkylene bridge which is interrupted by O, S or NR⁹,

R¹, R², R³, R⁴, R⁵, R⁶, R⁷ and R⁸ are, independently of one another hydrogen, alkyl, cycloalkyl, aryl, alkoxy, halogen, trifluoromethyl, nitro, alkoxy carbonyl or cyano.

In particular, the phosphinamidite ligand is selected from among the ligands of the formulae IIIa to IIIi

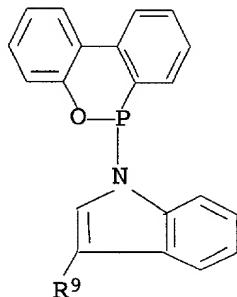
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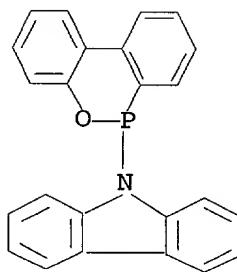


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(IIIa)



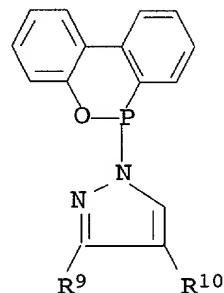
(IIIb)



(IIIc)

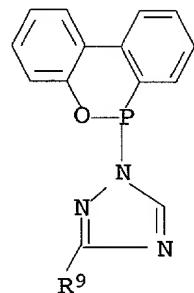
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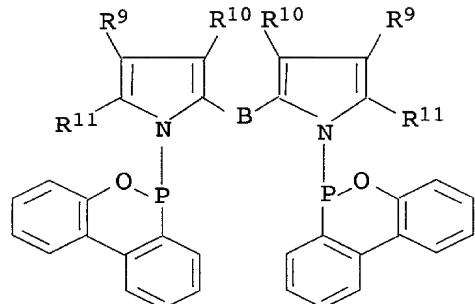
(IIId)



(IIIE)

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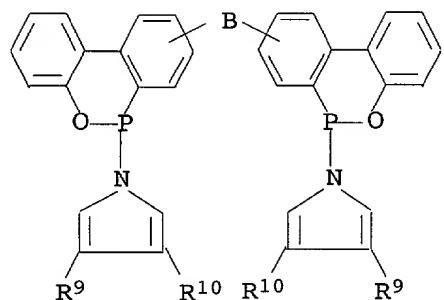


(IIIf)

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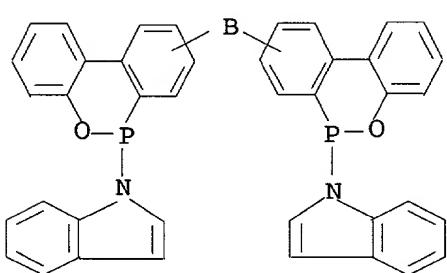


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(IIIg)

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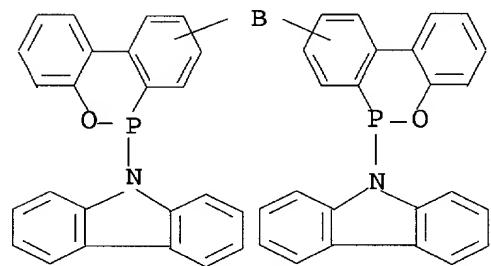


25

(IIIf)

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40

(IIIIi)

where

45 R⁹ and R¹⁰ are, independently of one another, hydrogen, methyl, ethyl or trifluoromethyl,

R¹¹ is hydrogen or COOC₂H₅,

B is CH₂, C(CH₃)₂, (CO)-(CO) or (CO)-D-(CO),

5 where B in the formulae IIIg, IIIh and IIIi can in each case be bound in the o,o positions, m,m positions or p,p positions relative to the phosphorus atoms and

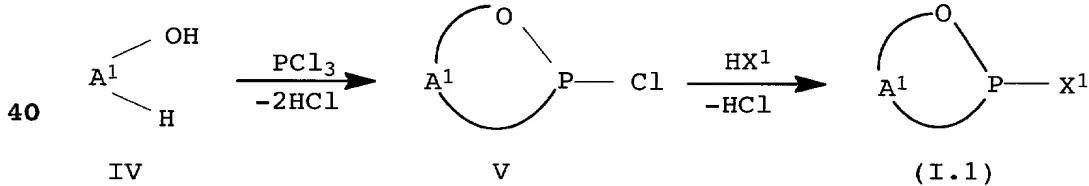
10 D is a C₁-C₁₀-alkylene bridge which may have one, two, three or four double bonds and/or be substituted and/or interrupted by substituted or unsubstituted heteroatoms as described above and/or have aryl and/or hetaryl groups fused onto it.

15 The catalysts of the present invention may have one or more phosphonamidite ligands of the formulae I.1, I.2 and I.3. In addition to the above-described ligands of the formulae I.1, I.2 and I.3 they may also bear at least one further ligand selected from among halides, amines, carboxylates, acetylacetone,

20 arylsulfonates or alkylsulfonates, hydride, CO, olefins, dienes, cycloolefins, nitriles, N-containing heterocycles, aromatics and heteraromatics, ethers, PF₃ and monodentate, bidentate and multidentate phosphine, phosphinite, phosphonite and phosphite ligands. These further ligands can likewise be monodentate,

25 bidentate or multidentate and coordinate to the metal atom of the catalyst complex. Suitable further phosphorus-containing ligands are, for example, customary phosphine, phosphonite and phosphite ligands.

30 The phosphinamidite ligands of the formula I.1 used according to the present invention can be prepared, for example, by reacting a hydroxyl group-containing compound of the formula IV with a phosphorus trihalide, preferably PCl₃, to give a compound of the formula V and then reacting this with a compound HX¹ containing at 35 least one secondary amino group, as shown in the following scheme



where A¹ and X¹ are as defined above.

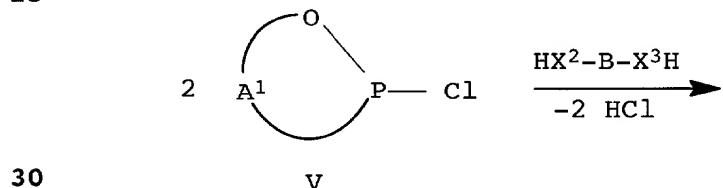
Examples of suitable compounds of the formula IV are biphenyl-2-ol, binaphthyl-2-ol, 1,1'-biphenyl-4-phenyl-2-ol, 1,1'-biphenyl-3,3',5,5'-tetra-t-butyl-2-ol, 1,1'-biphenyl-3,3'-di-t-amyl-5,5'-dimethoxy-2-ol, 1,1'-biphenyl-3,3'-di-t-butyl-5,5'-dimethoxy-2-ol, 1,1'-biphenyl-3,3'-di-t-butyl-2-ol, 1,1'-biphenyl-3,3'-di-t-butyl-6,6'-dimethyl-2-ol, 1,1'-biphenyl-3,3',5,5'-tetra-t-butyl-6,6'-dimethyl-2-ol, 1,1'-biphenyl-3,3'-di-t-butyl-5,5'-di-t-butoxy-2-ol, 1,1'-biphenyl-3,3'-di-t-hexyl-5,5'-dimethoxy-2-ol,

10 1,1'-biphenyl-3-t-butyl-5,5'-dimethoxy-2-ol, 1,1'-biphenyl-3,3'-di[2-(1,3-dioxacyclohexane)]-5,5'-dimethoxy-2-ol, 1,1'-biphenyl-3,3'-diformal-5,5'-dimethoxy-2-ol and 1,1'-biphenanthren-2-ol, in particular biphenyl-2-ol and binaphthyl-2-ol.

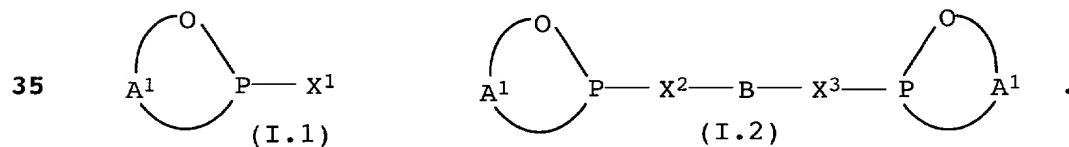
15 Examples of suitable compounds HX^1 are pyrrole, pyrazole, imidazole, 1-triazole, indole, indazole, purine, isoindole and carbazole.

The phosphinamidite ligands of the formula I.2 used according to 20 the present invention can be prepared, for example, by reacting two mol of at least one compound of the formula V with one mol of a compound HX^2-B-X^3H , where X^2 , X^3 and B are as defined above and the compound contains at least two secondary amino groups, as shown in the following scheme

25



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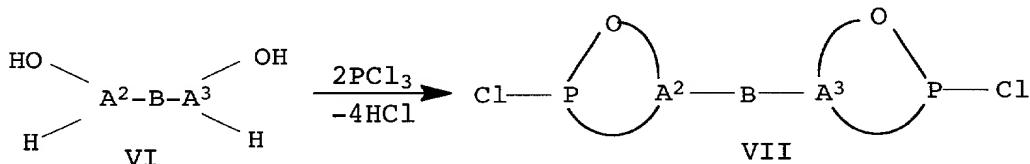
When using only one compound of the formula V, this reaction 40 gives phosphinamidite ligands having two identical phosphinamidite groups. However, if desired, two different compounds of the formula V can also be bridged by a compound HX^2-B-X^3H .

Suitable amines of the formula HX^2-B-X^3H are, for example, 45 customary alkylene-bridged bispyrroles and diacyl-bridged bispyrroles known to those skilled in the art.

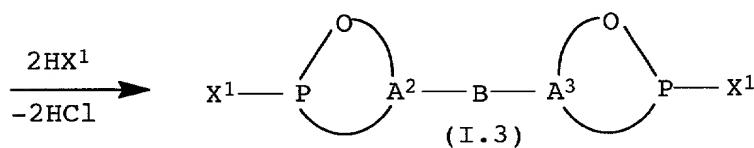
A method of preparing these ligands is described in DE-A-195 21 340, US 5,739,372 and in *Phosphorus and Sulfur*, 1987, Vol. 31, p. 71 ff for the formation of 6H-dibenz[c,e][1,2]oxaphosphorin ring systems. These documents 5 are hereby fully incorporated by reference.

The phosphinamidite ligands of the formula I.3 used according to the present invention can be prepared, for example, by reacting a compound of the formula VI containing two hydroxyl groups with a 10 phosphorus trihalide, preferably PCl_3 , to give a compound of the formula VII and then reacting this with at least one compound HX^1 , as described above for the preparation of the phosphinamidite ligands of the formula I.1, as shown in the following scheme

15



20



25

where A^2 , A^3 and X^1 are as defined above. If desired, two different compounds HX^1 can also be used for preparing the compounds of the formula I.3.

30

The compounds of the formulae V and VII may, if desired, be isolated and purified by known methods, e.g. distillation, crystallization, chromatography and the like.

35

The reaction of compounds of the formula IV to form compounds of the formula V and of compounds of the formula VI to form compounds of the formula VII generally proceeds at an elevated temperature in the range from about 40 to about 200°C; the reaction can also be carried out with a gradual increase in temperature. In addition, a Lewis acid such as zinc chloride or 40 aluminum chloride can be added as catalyst at the beginning of the reaction or after a certain reaction time. The further reaction of compounds of the formulae V and VII to give the phosphinamidite ligands of the formulae I.1, I.2 and I.3 used according to the present invention is generally carried out in 45 the presence of a base, e.g. an aliphatic amine such as diethylamine, dipropylamine, dibutylamine, trimethylamine, tripropylamine and preferably triethylamine or pyridine. The

preparation can also be carried out by deprotonation of the nitrogen heterocycle using a base and subsequent reaction with a compound of the formula V or VII. Bases suitable for the deprotonation are, for example, alkali metal hydrides, preferably 5 sodium hydride and potassium hydride, alkali metal amides, preferably sodium amide, lithium diisopropylamide, n-butyllithium, etc.

The preparation of the phosphinamidite ligands used according to 10 the present invention advantageously proceeds without use of organomagnesium or organolithium compounds. The simple reaction sequence allows wide variation of the ligands. The preparation can thus be carried out efficiently and economically from readily available starting materials.

15

In general, the catalysts or catalyst precursors used in each case form catalytically active species of the formula $H_xM_y(CO)_zL_q$, where M is a metal of transition group VIII, L is a phosphinamidite ligand used according to the present invention 20 and q, x, y, z are integers which depend on the valence and type of metal and on the number of co-ordination positions occupied by the ligand L, under hydroformylation conditions. Preferably, z and q are, independently of one another, at least 1, e.g. 1, 2 or 3. The sum of z and q is preferably from 2 to 5. The complexes 25 can, if desired, additionally contain at least one of the above-described further ligands.

The metal M is preferably cobalt, ruthenium, rhodium, nickel, palladium, platinum, osmium or iridium, in particular cobalt, 30 ruthenium, iridium, rhodium, nickel, palladium or platinum.

In a preferred embodiment, the hydroformylation catalysts are prepared in situ in the reactor used for the hydroformylation reaction. However, the catalysts of the present invention can, if 35 desired, also be prepared separately and isolated by customary methods. For the in-situ preparation of the catalysts of the present invention, it is possible, for example, to react at least one phosphinamidite ligand of the formulae I.1, I.2 and/or I.3, a compound or a complex of a metal of transition group VIII, if 40 desired at least one further additional ligand and, if desired, an activator in an inert solvent under the hydroformylation conditions.

Suitable rhodium compounds or complexes are, for example, 45 rhodium(II) and rhodium(III) salts such as rhodium(III) chloride, rhodium(III) nitrate, rhodium(III) sulfate, potassium rhodium sulfate, rhodium(II) or rhodium(III) carboxylate, rhodium(II) and

rhodium(III) acetate, rhodium(III) oxide, salts of rhodic(III) acid, trisammonium hexachlororhodate(III) etc. Also suitable are rhodium complexes such as biscarbonyl rhodium acetylacetone, acetylactonatobisethylenerhodium(I) etc. Preference is given to 5 using biscarbonyl rhodium acetylacetone or rhodium acetate.

Ruthenium salts or compounds are likewise suitable. Suitable ruthenium salts are, for example, ruthenium(III) chloride, ruthenium(IV), ruthenium(VI) or ruthenium(VIII) oxide, alkali 10 metal salts of oxo acids of ruthenium, e.g. K_2RuO_4 or $KRuO_4$ or complexes such as $RuHCl(CO)(PPh_3)_3$. It is also possible to use metal carbonyls of ruthenium such as dodecacarbonyltriruthenium or octadecacarbonylhexaruthenium, or mixed forms in which CO is partially replaced by ligands of the formula PR_3 , e.g. 15 $Ru(CO)_3(PPh_3)_2$, in the process of the present invention.

Examples of suitable cobalt compounds are cobalt(II) chloride, cobalt(II) sulfate, cobalt(II) carbonate, cobalt(II) nitrate, their amine or hydrate complexes, cobalt carboxylates such as 20 cobalt acetate, cobalt ethylhexanoate, cobalt naphthanoate, and also the cobalt caprolactamate complexes. Here too, the carbonyl complexes of cobalt, e.g. octacarbonyldicobalt, dodecacarbonyltetracobalt and hexadecacarbonylhexacobalt, can be used.

25 The abovementioned and further suitable compounds of cobalt, rhodium, ruthenium and iridium are known in principle and are adequately described in the literature, or they can be prepared by a person skilled in the art using methods analogous to those 30 for the known compounds.

Suitable activators are, for example, Brönsted acids, Lewis acids, such as BF_3 , $AlCl_3$, $ZnCl_2$, and Lewis bases.

35 As solvent, preference is given to using the aldehydes which are formed in the hydroformylation of the respective olefins and also their higher-boiling downstream reaction products, e.g. the products of the aldolcondensation. Further solvents which are likewise suitable are aromatics such as toluene and xylenes, 40 hydrocarbons or mixtures of hydrocarbons, including for dilution of the abovementioned aldehydes and the downstream products of the aldehydes. In the case of sufficiently hydrophilic ligands, it is also possible to use water, alcohols such as methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, ketones, 45 such as acetone and methyl ethyl ketone etc.

The molar ratio of phosphinamidite ligand to metal of transition group VIII is generally in a range from about 1:1 to 1,000:1.

The present invention further provides a process for the

5 hydroformylation of compounds containing at least one ethylenically unsaturated double bond by reaction with carbon monoxide and hydrogen in the presence of at least one of the hydroformylation catalysts of the present invention.

10 Suitable substrates for the hydroformylation process of the present invention are, in principle, all compounds which contain one or more ethylenically unsaturated double bonds. These include, for example, olefins such as α -olefins, internal straight-chain and internal branched olefins. Suitable α -olefins

15 are, for example, ethylene, propene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, etc.

Preferred straight-chain internal olefins are C₄-C₂₀-olefins, such as 2-butene, 2-pentene, 2-hexene, 3-hexene, 2-heptene, 3-heptene, 2-octene, 3-octene, 4-octene, etc.

Preferred branched, internal olefins are C₄-C₂₀-olefins such as 2-methyl-2-butene, 2-methyl-2-pentene, 3-methyl-2-pentene,

25 branched, internal heptene mixtures, branched, internal octene mixtures, branched, internal nonene mixtures, branched, internal dodecene mixtures, branched, internal undecene mixtures, branched, internal dodecene mixtures, etc.

30 Further suitable olefins for the hydroformylation reaction are C₅-C₈-cycloalkenes, such as cyclopentene, cyclohexene, cycloheptene, cyclooctene and their derivatives, for example, their C₁-C₂₀-alkyl derivatives having from 1 to 5 alkyl substituents. Additional olefins which are suitable for the

35 hydroformylation reaction are vinyl aromatics such as styrene, α -methylstyrene, 4-isobutylstyrene, etc. Other olefins which are suitable for the hydroformylation reaction are α,β -ethylenically unsaturated monocarboxylic and/or dicarboxylic acids, their esters, monoesters and amides, for example acrylic acid,

40 methacrylic acid, maleic acid, fumaric acid, crotonic acid, itaconic acid, methyl 3-pentenoate, methyl 4-pentenoate, methyl oleate, methyl acrylate, methyl methacrylate, and saturated nitriles such as 3-pentenenitrile, 4-pentenenitrile, acrylonitrile, vinyl ethers such as vinyl methyl ether, vinyl

45 ethyl ether, vinyl propyl ether, etc. C₁-C₂₀-alkenols, -alkenediols and -alkadienols such as 2,7-octadien-1-ol. Further suitable substrates are dienes or polyenes having isolated or

conjugated double bonds. These include, for example, 1,3-butadiene, 1,4-pentadiene, 1,5-hexadiene, 1,6-heptadiene, 1,7-octadiene, vinylcyclohexene, dicyclopentadiene, 1,5,9-cyclooctatriene and homopolymers and copolymers of

5 butadiene.

Preference is given to a process in which the hydroformylation catalyst is prepared in situ by reacting at least one phosphinamidite ligand as is used according to the present 10 invention, a compound or a complex of a metal of transition group VIII and, if desired, an activator in an inert solvent under the hydroformylation conditions.

The hydroformylation reaction can be carried out continuously, 15 semicontinuously or batchwise.

Suitable reactors for the continuous reaction are known to those skilled in the art and are described, for example, in Ullmanns Enzyklopädie der technischen Chemie, Vol. 1, 3. 3rd Edition, 20 1951, p. 743 ff.

Suitable pressure-rated reactors are likewise known to those skilled in the art and are described, for example, in Ullmanns Enzyklopädie der technischen Chemie, Vol. 1, 3. 3rd Edition, 25 1951, p. 769 ff. In general, the process of the present invention is carried out using an autoclave which may, if desired, be provided with a stirring apparatus and an interior lining.

The composition of the synthesis gas (carbon monoxide and 30 hydrogen) used in the process of the present invention can vary within wide limits. The molar ratio of carbon monoxide and hydrogen is generally from about 5:95 to 70:30, preferably from about 40:60 to 60:40. Particular preference is given to using a molar ratio of carbon monoxide and hydrogen in the region of 35 about 1:1.

The temperature of the hydroformylation reaction is generally in a range from about 20 to 180 °C, preferably from about 50 to 40 150°C. The reaction is generally carried out at the partial pressure of the reaction gas at the reaction temperature selected. In general, the pressure is in a range from about 1 to 700 bar, preferably from 1 to 600 bar, in particular from 1 to 300 bar. The reaction pressure can be varied as a function of the activity of the novel hydroformylation catalyst used. In general, 45 the novel catalysts based on phosphinamidite ligands allow a

reaction in a low pressure range, for example in a range from 1 to 100 bar.

The hydroformylation catalysts of the present invention can be 5 separated from the reaction product of the hydroformylation reaction by customary methods known to those skilled in the art and can generally be reused for the hydroformylation.

The catalysts of the present invention advantageously display a 10 high activity, so that the corresponding aldehydes are generally obtained in good yields. In the hydroformylation of α -olefins and of internal, linear olefins, they additionally display a very low selectivity to the hydrogenation product of the olefin used.

15 The above-described, novel catalysts which comprise chiral phosphinamidite ligands are suitable for enantioselective hydroformylation.

The present invention further provides for the use of catalysts 20 comprising one of the above-described phosphinamidite ligands for the hydroformylation of compounds having at least one ethylenically unsaturated double bond.

A further field of application for the catalysts of the present 25 invention is the hydrocyanation of olefins. The hydrocyanation catalysts of the present invention also comprise complexes of a metal of transition group VIII, in particular cobalt, nickel, ruthenium, rhodium, palladium, platinum, preferably nickel, palladium and platinum and very particularly preferably nickel.

30 In general, the metal is present in zero-valent form in the metal complex of the present invention. The preparation of the metal complexes can be carried out as described above for use as hydroformylation catalysts. The same applies to the in-situ preparation of the hydrocyanation catalysts of the present 35 invention.

A nickel complex suitable for preparing a hydrocyanation catalyst is, for example, bis(1,5-cyclooctadiene)nickel(0).

40 If desired, the hydrocyanation catalysts can be prepared in situ using a method analogous to that described for the hydroformylation catalysts.

The present invention therefore also provides a process for 45 preparing nitriles by catalytic hydrocyanation in which the hydrocyanation is carried out in the presence of at least one of the above-described catalysts of the present invention. Suitable

olefins for the hydrocyanation are generally the olefins mentioned above as starting materials for the hydroformylation. A specific embodiment of the process of the present invention relates to the preparation of mixtures of monoolefinic

5 C_5 -mononitriles having nonconjugated $C=C$ - and $C\equiv N$ bonds by catalytic hydrocyanation of 1,3-butadiene or 1,3-butadiene-containing hydrocarbon mixtures and isomerization/further reaction to form saturated C_4 -dinitriles, preferably adiponitrile, in the presence of at least one catalyst

10 according to the present invention. When using hydrocarbon mixtures for preparing monoolefinic C_5 -mononitriles by the process of the present invention, preference is given to using a hydrocarbon mixture which has a 1,3-butadiene content of at least 10% by volume, preferably at least 25% by volume, in particular 15 at least 40% by volume.

1,3-butadiene-containing hydrocarbon mixtures are obtainable on an industrial scale. Thus, for example, the refining of petroleum by steam cracking of naphtha produces a hydrocarbon mixture, 20 known as C_4 fraction, where about 40% is 1,3-butadiene and the remainder is monoolefins and multiply unsaturated hydrocarbons together with alkanes. These streams always also contain small amounts of generally up to 5% of alkynes, 1,2-dienes and vinylacetylene.

25 Pure 1,3-butadiene can be isolated from industrially available hydrocarbon mixtures by, for example, extractive distillation.

The catalysts of the present invention can be advantageously used 30 for the hydrocyanation of such olefin-containing, in particular 1,3-butadiene-containing, hydrocarbon mixtures, generally even without prior purification of the hydrocarbon mixture by distillation. Any olefins present which impair the effectiveness of the catalysts, e.g. alkynes or cumulenes, can, if necessary be 35 removed from the hydrocarbon mixture by selective hydrogenation prior to the hydrocyanation. Suitable processes for selective hydrogenation are known to those skilled in the art.

The hydrocyanation of the present invention can be carried out 40 continuously, semicontinuously or batchwise. Suitable reactors for the continuous reaction are known to those skilled in the art and are described, for example, in Ullmanns Enzyklopädie der technischen Chemie, Vol. 1, 3rd Edition, 1951, p. 743 ff. The continuous variant of the process of the invention is preferably 45 carried out using a cascade of stirred tanks or a tube reactor. Suitable reactors, which may be pressure rated, for the semicontinuous or continuous process are known to those skilled

in the art and are described, for example, in Ullmanns Enzyklopädie der technischen Chemie, Vol. 1, 3rd Edition, 1951, p. 769 ff. The process of the present invention is generally carried out using an autoclave which may, if desired, be provided 5 with a stirring apparatus and an interior lining.

The hydrocyanation catalysts can be separated from the reaction product of the hydrocyanation reaction by customary methods known to those skilled in the art and can generally be reused for the 10 hydrocyanation.

The invention is illustrated by the following, non-restrictive examples.

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Examples

The ligands described below can, if desired, be further purified by customary purification methods known to those skilled in the 20 art, for example crystallization and distillation.

A) Preparation of the ligands IIIa to IIIc

Example 1:

25 Preparation of ligand IIIa

206 g (1.5 mol) of phosphorus trichloride and 204 g (1.2 mol) of biphenyl-2-ol are, while stirring in an argon atmosphere, slowly heated to 50°C and then heated further to 140°C over a period of 8 30 hours. Vigorous hydrogen chloride evolution occurs and the solution becomes yellow. After cooling to 120°C, a catalytic amount of zinc chloride (1.2 g; 17 mmol) is added and the mixture is heated at 140°C for 24 hours. On subsequent distillation, the reaction product 6-chloro-(6H)-dibenz[c,e][1,2]oxaphosphorin goes 35 over at a boiling point of 132°C (0.2 mbar).

Yield: 194.8 g (69%) of white crystals;

^{31}P -NMR spectrum: δ (ppm) 134.5.

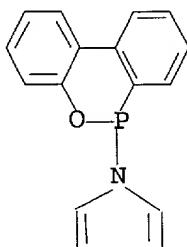
Further methods of preparing 6-chloro-(6H)-dibenz[c,e][1,2]-40 oxaphosphorin are described in DE-A-20 34 887 and EP-A-0 582 957.

2.9 g of potassium hydride (35% strength suspension in mineral oil; 25 mmol) and 80 ml of tetrahydrofuran are placed under an argon atmosphere in a reaction vessel. 1.75 g (26 mmol) of 45 pyrrole are then slowly added dropwise, with the temperature rising to about 33°C. After hydrogen evolution has stopped, 6 g (26 mmol) of 6-chloro-(6H)-dibenz[c,e][1,2]oxaphosphorin is added

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as a solution in 40 ml of tetrahydrofuran and the mixture is subsequently stirred for 12 hours at room temperature. The mixture is evaporated to dryness, taken up in toluene and filtered through a 2 cm kieselguhr column. Evaporation of the solvent gives the ligand IIIa as a white solid.

10



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(IIIa)

20 Yield: 3.3 g (50 %) of white crystals;

^{31}P -NMR spectrum (CDCl_3): δ (ppm) 77.2

^1H -NMR spectrum: corresponds to the proposed structure

An alternative method of preparing ligand IIIa is to place 9.7 g (36.6 mmol) of 6-chloro-(6H)-dibenz[c,e][1,2]oxaphosphorin as a solution in 80 ml of toluene in a reaction vessel, subsequently to add 4.9 g (73.2 mmol) of pyrrole and then to slowly add 7.6 g (75 mmol) of triethylamine dropwise at room temperature, immediately forming a mist of triethylamine hydrochloride. The mixture is stirred for 6 hours at 70°C and subsequently for 12 hours at room temperature. After filtration, the resulting filtrate is evaporated to dryness, the residue is taken up in methyl tert-butyl ether and subsequently precipitated by cooling to -30°C.

35 Yield: 6.7 g (72%);

^{31}P -NMR spectrum (CDCl_3): as above

^1H -NMR spectrum: corresponds to the proposed structure

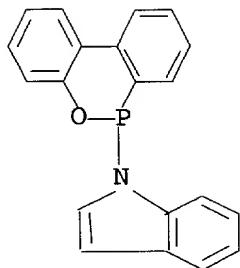
Example 2:

40 Preparation of ligand IIIb

The ligand IIIb is prepared using a method analogous to that described in Example 1 by reacting 6-chloro-(6H)-dibenz[c,e][1,2]oxaphosphorin with indol and 45 triethylamine as base. The product obtained is purified by washing with water and recrystallization from acetonitrile.

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(IIIb)

15 ^{31}P -NMR spectrum (CDCl_3): δ (ppm) 66.7 ^1H -NMR spectrum: corresponds to the proposed structure

Example 3:

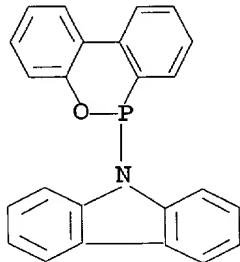
Preparation of ligand IIIc

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The ligand IIIc is prepared using a method analogous to that described in Example 1 by reacting 6-chloro-(6H)-dibenz[c,e][1,2]oxaphosphorin with carbazole and triethylamine as base.

25

30



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(IIIc)

31 ^{31}P -NMR spectrum (CDCl_3): δ (ppm) 81.440 ^1H -NMR spectrum: corresponds to the proposed structure

B) Hydroformylations

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Example 4:

Hydroformylation of 1-octene

5 In a 300 ml steel autoclave fitted with sparging stirrer, 123 mg of biscarbonylrhodium acetylacetone, 680 mg of ligand IIIa, 22.5 g of 1-octene and 25 ml of Texanol® (solvent based on 2,2,4-trimethylpentane-1,3-diol monoisobutyrate) were reacted at 100°C under a protective argon atmosphere with a synthesis gas mixture of CO/H₂ (1:1) at 40 bar (108 ppm of Rh; ligand/metal ratio = 54). After a reaction time of 4 hours, the autoclave was vented and emptied. The mixture was analyzed by means of gas chromatography (GC) using an internal standard. The conversion was 100%, the selectivity in respect of the nonanal isomers was 96% and the proportion of n-isomer was 80%.

Example 5:

Hydroformylation of 1-octene

20 The procedure of Example 4 was repeated using 134 mg of biscarbonylrhodium acetylacetone, 310 mg of ligand IIIb, 22.5 g of 1-octene and 25 ml of Texanol® for the hydroformylation (118 ppm of Rh; ligand/metal ratio = 19). The conversion was 99%, the selectivity in respect of nonanal isomers was 88% and the proportion of n-isomer was 68%.

Example 6:

Hydroformylation of 1-octene

30 The procedure of Example 4 was repeated using 12.4 mg of biscarbonylrhodium acetylacetone, 480 mg of ligand IIIc, 22.5 g of 1-octene and 22.5 g of Texanol® for the hydroformylation (109 ppm of Rh; ligand/metal ratio = 45). The conversion was 99%, the selectivity in respect of nonanal isomers was 82% and the proportion of n-isomer was 51%.

Example 7:

Hydroformylation of 3-pentene nitrile

40 The general procedure of Example 4 was repeated using 6.2 mg of biscarbonylrhodium acetylacetone, 322 mg of ligand IIIa, 10 g of 3-pentenenitrile and 15 g of xylene at a temperature of 110°C, a pressure of 80 bar and a reaction time of 4 h for the hydroformylation (100 ppm of Rh; ligand/metal ratio = 50). The conversion was 69% and the selectivity in respect of 3-formylvaleronitrile was 65%, that in respect of

25

4-formylvaleronitrile was 24% and that in respect of 5-formylvaleronitrile was 4%.

Example 8:

5

Hydroformylation of 3-pentenenitrile

The general procedure of Example 4 was repeated using 6.2 mg of bis(biscarbonylrhodium acetylacetone), 382 mg of ligand IIIb, 10 g of 3-pentenenitrile and 15 g of xylene at a temperature of 110°C, a pressure of 70 bar and a reaction time of 4 h for the hydroformylation (100 ppm of Rh; ligand/metal ratio = 50). The conversion was 99% and the selectivity in respect of 3-formylvaleronitrile was 59%, that in respect of 4-formylvaleronitrile was 30% and that in respect of 5-formylvaleronitrile was 9%.

Example 9:

20 Hydroformylation of 3-pentenenitrile

The general procedure of Example 4 was repeated using 6.2 mg of bis(biscarbonylrhodium acetylacetone), 443 mg of ligand IIIc, 10 g of 3-pentenenitrile and 15 g of xylene at a temperature of 110°C, a pressure of 70 bar and a reaction time of 4 h for the hydroformylation (100 ppm of Rh; ligand/metal ratio = 50). The conversion was 80% and the selectivity in respect of 3-formylvaleronitrile was 41%, that in respect of 4-formylvaleronitrile was 38% and that in respect of 5-formylvaleronitrile was 18%.

Example 10

Hydroformylation of octene-N

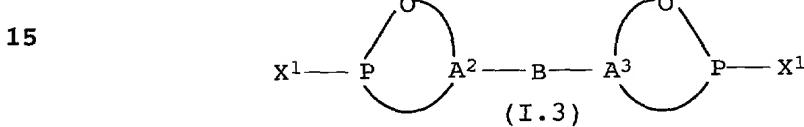
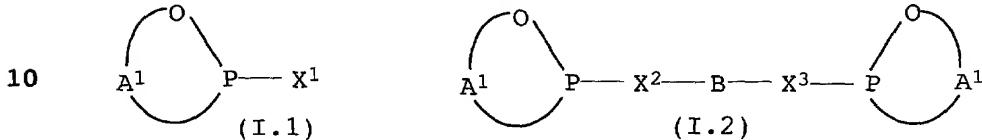
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The general procedure of Example 4 was repeated using 126 mg of bis(biscarbonylrhodium acetylacetone), 270 mg of ligand IIIa, 22.5 g of octene-N and 22.5 g of Texanol® at a temperature of 130°C, a pressure of 60 bar and a reaction time of 6 h for the hydroformylation (111 ppm of Rh; ligand/metal ratio = 20). The conversion was 59% and the selectivity in respect of nonanal isomers was 85% and that in respect of nonanol isomers was 11%.

45

We claim:

1. A catalyst comprising at least one complex of a metal of
 5 transition group VIII comprising at least one monodentate,
 bidentate or multidentate phosphinamidite ligand of the
 formulae I.1, I.2 and/or I.3



where

20 A^1 together with the phosphorus atom and the oxygen atom to which it is bound form a 5- to 8-membered heterocycle onto which one, two or three cycloalkyl, aryl and/or hetaryl groups may be fused, where the fused-on groups may each bear, independently of one another, one, two or three substituents selected from among alkyl, alkoxy, halogen, nitro, cyano, carboxyl and carboxylate,

25 A^2 and A^3 are, independently of one another, part of a heterocycle as defined for A^1 which is substituted by B,

30 X^1 is a 5- to 8-membered heterocycle which contains at least one nitrogen atom bound directly to the phosphorus atom, where the heterocycle may additionally contain one or two heteroatom(s) selected from among N, O and S and/or one, two or three cycloalkyl, aryl and/or hetaryl groups may be fused onto the heterocycle, where the heterocycle and/or the fused-on groups may each bear, independently of one another, one, two or three substituents selected from among alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy, aryloxy, acyl, halogen, trifluoromethyl, nitro, cyano, carboxyl, carboxylate, alkoxy carbonyl and NE^1E^2 , where E^1 and E^2 may be identical or different and are each alkyl, cycloalkyl or aryl,

35 X^2 and X^3 are, independently of one another, a heterocycle as defined for X^1 which is substituted by B,

40 X^2 and X^3 are, independently of one another, a heterocycle as defined for X^1 which is substituted by B,

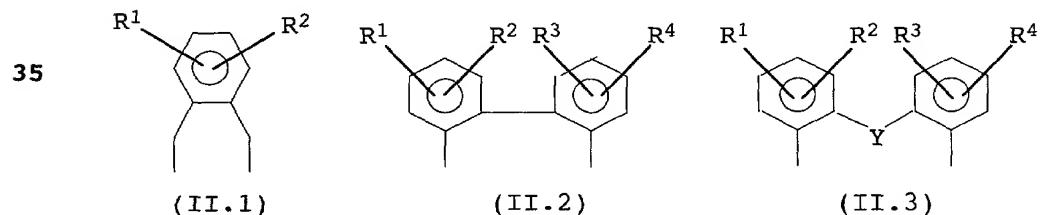
45 X^2 and X^3 are, independently of one another, a heterocycle as defined for X^1 which is substituted by B,

B is either a carbon-carbon single bond or a divalent bridging group,
 5 or salts or mixtures thereof.

2. A catalyst as claimed in claim 1, wherein B is a bridging group of the formula -D-, -(CO)-D-(CO)- or -(CO)-(CO)-, in
 10 which

D is a C₁-C₁₀-alkylene bridge which may have one, two,
 15 three or four double bonds and/or bear one, two, three or four substituents selected from among alkyl, alkoxy, halogen, nitro, cyano, carboxyl, carboxylate, cycloalkyl and aryl, where the aryl substituent may additionally bear one, two or three substituents selected from among alkyl, alkoxy, halogen, trifluoromethyl, nitro, alkoxy carbonyl or cyano, and/or the alkylene bridge D may be interrupted by one, two or three nonadjacent, substituted or unsubstituted heteroatoms, and/or the alkylene bridge D may have one, two or three aryl and/or hetaryl groups fused onto it, where the fused-on aryl and hetaryl groups may each bear one, two or three substituents selected from among alkyl, cycloalkyl, aryl, alkoxy, cycloalkoxy, aryloxy, aryl, halogen, trifluoromethyl, nitro, cyano, carboxyl, alkoxy carbonyl and NE¹E², where E¹ and E² may be identical or different and are each alkyl, cycloalkyl or aryl.

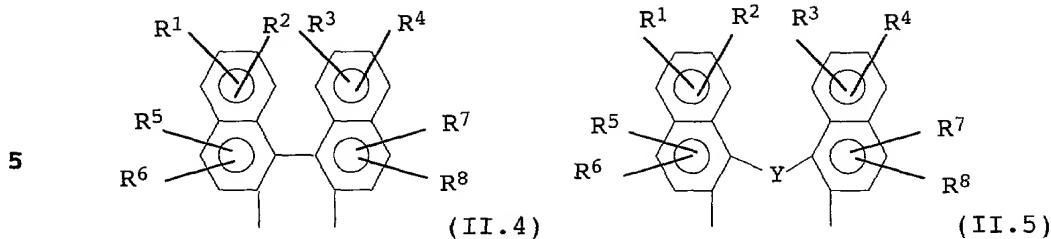
30 3. A catalyst as claimed in claim 2, wherein D is a radical of the formula II.1, II.2, II.3, II.4 or II.5



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45

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where

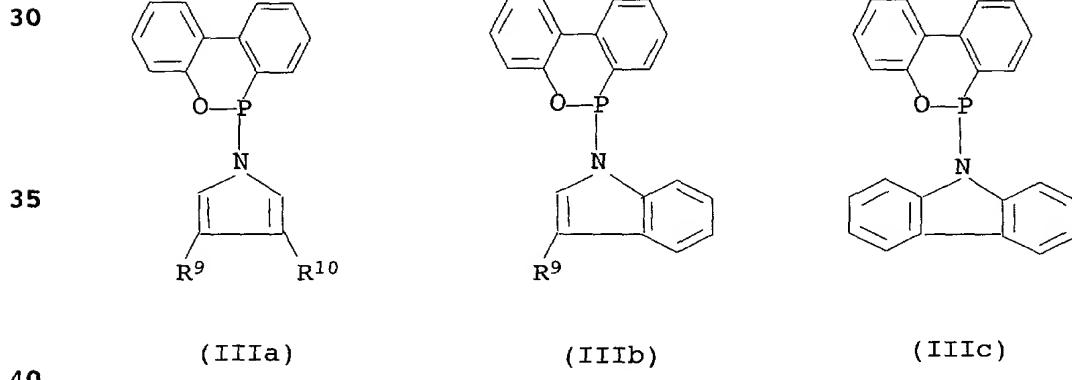
10 Y is O, S, NR⁹, where
R⁹ is alkyl, cycloalkyl or aryl,

15 or Y is a C₁-C₃-alkylene bridge which may have a double bond
and/or an alkyl, cycloalkyl- or aryl substituent, where the
aryl substituent may bear one, two or three substituents
selected from among alkyl, alkoxy, halogen, trifluoromethyl,
nitro, alkoxy carbonyl and cyano,

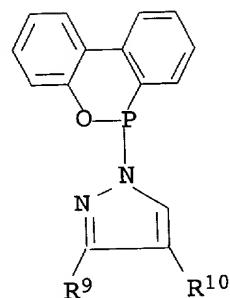
20 or Y is a C₂-C₃-alkylene bridge which is interrupted by O, S or
NR⁹,

25 R¹, R², R³, R⁴, R⁵, R⁶, R⁷ and R⁸ are, independently of one
another hydrogen, alkyl, cycloalkyl, aryl, alkoxy,
halogen, trifluoromethyl, nitro, alkoxy carbonyl or cyano.

4. A catalyst as claimed in any of the preceding claims, wherein
the phosphinamidite ligand is selected from among the ligands
of the formulae IIIa to IIIc

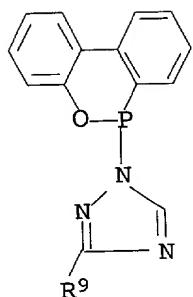


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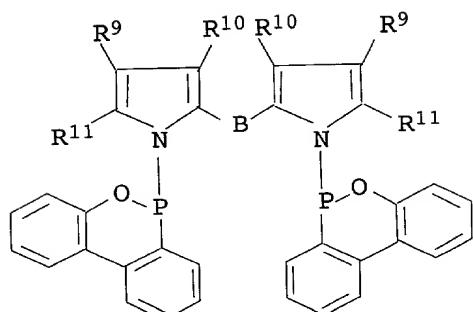
(IIIId)



(IIIe)

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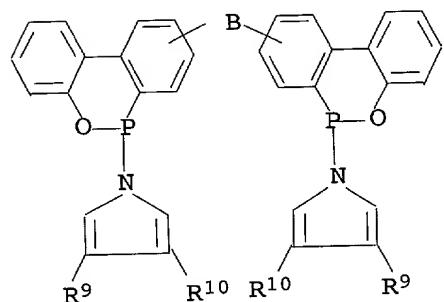
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(IIIf)

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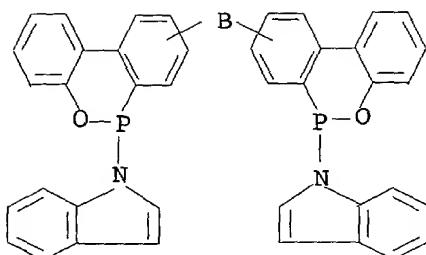
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(IIIfg)

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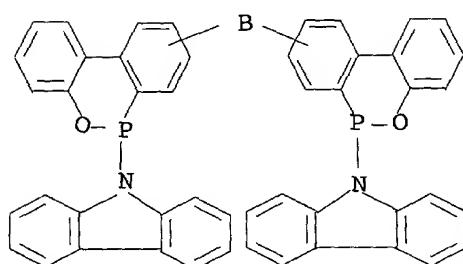


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(IIIh)

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(IIIf)

where

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R^9 and R^{10} are, independently of one another, hydrogen, methyl, ethyl or trifluoromethyl,

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R^{11} is hydrogen or $COOC_2H_5$,

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B is CH_2 , $C(CH_3)_2$, $(CO)-(CO)$ or $(CO)-D-(CO)$,

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where B in the formulae IIIf, IIIh and IIIf can in each case be bound in the σ,σ positions, π,π positions or ρ,ρ positions relative to the phosphorus atoms and

D is a C_1-C_{10} -alkylene bridge as defined in claim 2 or 3.

45 5. A catalyst as claimed in any of the preceding claims, wherein the metal of transition group VIII is selected from among cobalt, ruthenium, iridium, rhodium, nickel, palladium and

platinum.

6. A catalyst as claimed in any of the preceding claims which further comprises at least one further ligand selected from
5 among halides, amines, carboxylates, acetylacetone, arylsulfonates or alkylsulfonates, hydride, CO, olefins, dienes, cycloolefins, nitriles, N-containing heterocycles, aromatics and heteroaromatics, ethers, PF₃ and monodentate, bidentate and multidentate phosphine, phosphinite,
10 phosphonite and phosphite ligands.
7. A process for the hydroformylation of compounds which contain at least one ethylenically unsaturated double bond by reaction with carbon monoxide and hydrogen in the presence of
15 a hydroformylation catalyst, wherein the hydroformylation catalyst used is a catalyst as claimed in any of claims 1 to 6.
8. A process for the hydrocyanation of compounds containing at
20 least one ethylenically unsaturated double bond by reaction with hydrogen cyanide in the presence of a hydrocyanation catalyst, wherein the hydrocyanation catalyst used is a catalyst as claimed in any of claims 1 to 6.
- 25 9. A process as claimed in claim 7 or 8, wherein the hydroformylation catalyst or the hydrocyanation catalyst is prepared in situ by reacting at least one phosphinamidite ligand as defined in any of claims 1 to 6, a compound or a complex of a metal of transition group VIII and, if desired,
30 an activator in an inert solvent under the hydroformylation conditions or the hydrocyanation conditions.
10. The use of a catalyst comprising a phosphinamidite ligand as claimed in any of claims 1 to 6 for the hydroformylation or
35 hydrocyanation of compounds having at least one ethylenically unsaturated double bond.

Catalyst comprising a complex of a metal of transition group VIII based on a phosphinamidite ligand

Abstract

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A catalyst comprising at least one complex of a metal of transition group VIII comprising at least one monodentate, bidentate or multidentate phosphinamidite ligand in which the phosphorus atom and the oxygen atom of the phosphinamidite group 10 form part of a 5- to 8-membered heterocycle can be used for the hydroformylation and hydrocyanation of compounds containing at least one ethylenically unsaturated double bond.

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Declaration

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0050/049849

We (I) hereby claim the benefit under Title 35, United States Codes, § 119(e) of any United States provisional application(s) listed below.

(Application Number)	(Filing Date)
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(Application Number)	(Filing Date)
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We (I) hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

Application Serial No.	Filing Date	Status (pending, patented, abandoned)
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

And we (I) hereby appoint **Messrs. HERBERT. B. KEIL**, Registration Number 18,967; and **RUSSEL E. WEINKAUF**, Registration Number 18,495; the address of both being Messrs. Keil & Weinkauf, 1101 Connecticut Ave., N.W., Washington, D.C. 20036 (telephone 202-659-0100), our attorneys, with full power of substitution and revocation, to prosecute this application, to make alterations and amendments therein, to sign the drawings, to receive the patent, and to transact all business in the Patent Office connected therewith.

We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Declaration, Power of Attorney

(8)

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We (I), the undersigned inventor(s), hereby declare(s) that:

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Catalyst comprising a metal complex of the VIII subgroup based on a phosphine amidite ligand and its utilization for hydroformylation and hydrocyanation

the specification of which

[*] is attached hereto.

[] was filed on _____ as

Application Serial No. _____

and amended on _____.

[x] was filed as PCT international application

Number PCT/EP 00/ 02610

on March 23, 2000

and was amended under PCT Article 19

on _____ (if applicable).

We (I) hereby state that we (I) have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application(s)

Application No.	Country	Day/Month/Year	Priority Claimed
19913352.2	Germany	24 March 1999	[x] Yes [] No

Declaration

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